THE FUNCTION OF PEPTIZING PROTECTIVE COLLOID IN THE CASTING OF CLAY SLIPS

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DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

PAUL HERMAN MAUTZ, B.Sc. in Agr. and M.Sc.

L. C.

The Ohio State University
1928
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FOREWORD

A great many ceramic products in everyday use, such as lavatories and other sanitary ware, insulators and other electrical porcelain products, and some of the better grades of tableware are made by casting the slip or thick creamy ingredients in molds. Casting is used, also, to some extent in the making of heavy clay products. Two methods are used, single casting and solid casting.

In single casting the clay slip is poured into an open clay mold, and is allowed to set until a piece of the desired thickness is obtained. The excess slip is then poured out of the mold. Castings made in this way are usually not more than one-fourth inch in thickness.

For solid casting a mold containing a core is used, and the clay slip is filled solidly between the core and the wall of the mold. Solid casting is of great commercial importance, and as ways of obtaining more satisfactory results with the slips are developed this method is destined to increase in importance, particularly for sanitary ware. It is probable that already more than 50 per cent of all vitreous sanitary ware produced in the United States is manufactured by the solid casting process.

A greater and more successful use of solid casting would result if certain objections could be overcome. It would be desirable to cast thicker pieces than is at present possible. When pieces vary in thickness, inequality in time of setting of the various parts is objectionable. Studies that throw light on methods of obtaining such improvement in properties would be of great benefit to the ceramic industry. The present investigation has covered a study of the properties and methods of control of the casting slips and developed some modifications which should be of interest and practical value. This study was confined to slips typical of the whiteware industry.

The research reported in this bulletin was submitted by Mr. Mautz as his dissertation for the degree of doctor of philosophy.

Acknowledgment is due Dr. Edward Mack, professor of physical chemistry at the Ohio State University, and Mr. T. A. Klinefelter, superintendent of the Columbus Branch, United States Bureau of Standards, under whose direction the work of this project was performed.

E. A. HITCHCOCK, *Director.*

THE FUNCTION OF PEPTIZING PROTECTIVE COLLOID IN THE CASTING OF CLAY SLIPS

The problem of solid casting is of considerable interest to a number of ceramic industries. It is, however, subject to a number of severe limitations. Among these are the following: (1) present methods do not permit of casting thicknesses greater than ¾-inch satisfactorily; (2) inequality in thickness of cross-section causes trouble; and (3) it has been very difficult to obtain a satisfactory method of control whereby one can foretell whether or not a reasonably good cast can be made from the slip.

The present investigation was conducted primarily for the purpose of determining how different slip components function and to formulate a better method of control.

BRIEF SUMMARY

Practice in the ceramic industries has consisted to quite an extent in depending on organic matter in the clays used to furnish the desired characteristics in the slip. Such methods make the operations depend more on experience and approximation than on definite technical procedure.

From the experiments of this investigation it is believed that china clays and ball clays containing little or no organic matter, or china clays alone, should be used in casting slips, and that control may be obtained by casting test pieces in which the proportions of electrolyte and peptizing protective colloid are varied until the desired properties of the body are obtained.

FUNCTIONS OF DIFFERENT SLIP COMPONENTS: THEORIES OF SLIP FORMATION

A typical casting slip has the following composition:

China clay	40 per cent
Ball clay	10 per cent
Flint	30 per cent
Feldspar	20 per cent

Both sodium carbonate and sodium silicate are usually added in amounts equal to 0.125 per cent of the dry weight of the body. The body is stirred up with sufficient water to form a thick suspension. This suspension is known as the slip.

The flint and feldspar function as non-plastics in the casting process. They also accelerate the rate of setting by helping to maintain the open structure necessary for the drainage of the excess water from the slip to the mold.

It is generally believed that ball clays contribute the essential property of fluidity to the slip.[1] The dark English ball clays are generally more fluid than the light English ball clays. As soon as the mold has been filled, this valuable property of ball clays has largely played its part. They cannot be used alone because of their fine texture. When the piece begins to set, the finely dispersed particles are rapidly built up on the surface of the mold with sufficient density to prevent the passage of water from the center of the piece to the mold. A decreased rate of setting and the formation of sections of uneven density result. It therefore becomes necessary to introduce into the body a medium which will temper the influence of the ball clay. This is essentially the function of china clays. The property of china clays which is chiefly desired is proper setting behavior in the mold.

The function of the alkalies is to deflocculate the clay. Increasing proportions of the alkalies usually result in increased dispersion of the fine particles until a well-defined maximum is reached. Further additions of alkali then result in precipitation or coagulation of the material or an increase in the viscosity of the slip. The mechanism of the deflocculating action of alkalies on clays is variously explained. Neubert[2] is of the opinion that the clay particles adsorb the hydroxyl ions, and then repel one another. Bleininger[3] advances the view that the negatively charged hydroxyl ions repel the similarly charged clay particles electrostatically.

Neubert[2] advanced the first comprehensive theory of the liquefaction of clays by alkalies. He offers the following explanation of the liquefaction of clays by alkalies and of the curious phenomenon known as reliquefaction:

On the addition of an alkaline solution (of suitable concentration) to clay, the clay particles adsorb the hydroxyl ions and repel each other. The mass becomes fluid as a result of the increased mobility of the clay particles. After a time, stiffening, occasioned by the swelling of the clay particles, sets in. The humus substances contained in the clay also swell and are thereby empowered to form alkali humate. But only a very small amount of alkali can be removed from the adsorption equilibrium in this way, since the alkali humate formed is extensively hydrolyzed and again furnishes hydroxyl ions. As the alkali addition increases, its suspending effect becomes so marked that the stiffening resulting from swell-

[1] A. C. Gerber, "Casting Control," *Jour. Amer. Ceram. Soc.*, Vol. 8 (1925), p. 18.
[2] J. K. Neubert, "Die Tonverflüssigung durch Alkali," *Kolloidchem. Beihefte*, Vol. 4 (1912), p. 261.
[3] A. V. Bleininger, "Use of Sodium Salts in the Purification of Clays and in the Casting Process," Bur. Stand. *Tech. Paper*, No. 51.

ing becomes continually less perceptible. Liquefaction is also facilitated by splitting up of the clay particles which results from the solution of humus by the alkali. At the point of maximum liquefaction the two effects, swelling and splitting up of the clay particles, determine the equilibrium. But the splitting effect is not yet marked; it first appears prominently in the reliquefaction. If the alkali concentration is now raised above the optimum, coagulation of the individual particles occurs, and the slip stiffens. If a sufficiently high concentration of alkali is now used, the hydroxyl ions force the alkali humate, which has a protective effect, from the adsorbing surface. This should again lead to stiffening of the slip. But the high concentration of alkali provides the possibility of an increasingly extensive splitting of the clay particles. New adsorbing surfaces come into play, and the amount of alkali humate is increased. The clay is again gradually converted into the fluid condition. It is reliquefied. With further increase in alkali concentration, the reliquefaction gradually becomes less, since (1) the increase in the amount of alkali humate is limited by the humus content of the clay, (2) less alkali humate remains adsorbed with increasing hydroxyl ion concentration, and (3) the decrease in the amount of alkali humate at higher hydroxyl-ion concentrations as the result of the appearance of fresh surfaces will not necessitate a corresponding decrease in the amount of adsorbed hydroxyl ions. The clay slip will then remain stiff.

Bleininger[3] suggests that by the action of the alkali on the clay, the fine grains of clay already present may be still further subdivided into submicroscopic particles resulting in the formation of a certain amount of emulsoid-like substances. This "pseudo-emulsoid" may tend to hold up fine particles which would otherwise settle.

Other than the theories of Bleininger and Neubert there is very little information in the literature on the mechanism of the liquefaction and setting of clay slips. It seems more probable that the organic matter of the ball clay rather than the hypothetical "pseudoemulsoid" of Bleininger exerts a protective effect on the system.

In the Symposium on Casting Problems,[4] one of the questions was "What measures should be taken for correcting a slip that requires excessive electrolyte?" One of the participants in the discussion suggested lowering the ball clay to the amount of electrolyte required, since the electrolyte acts upon the plastic material of the ball clay. This suggestion was immediately opposed. It

[4] "Symposium on Casting Problems," *Jour. Amer. Ceram. Soc.*, Vol. 8 (1925), p. 565.

was claimed that ball clays are characteristically dispersed, whereas the English china clays are usually highly flocculated, and that the deflocculating action of the electrolyte must therefore be exerted upon the china clay rather than upon the ball clay. Several instances were then mentioned where the amount of electrolyte necessary had been greatly reduced by increasing the ball clay content of the slip. For instance, in casting electrical insulators, an increase in the amount of ball clay from 12 to 23 per cent decreased the amount of alkali necessary by about one-third. It was also noted that ball clays of relatively low organic content require more electrolyte than ball clays of relatively high organic content.

Sanborn[5] dispensed with electrolyte by using a Missouri clay containing humus. The viscosity of such slips gradually decreased. The initial viscosity of the slip was 180, the time of outflow of the slip being compared with the time of outflow of a similar volume of water. After aging for four days, the viscosity had fallen to about 125.

Scripture and Schramm[6] found that within the range of practical working compositions an increase in ball clay gave increased fluidity to the casting slips. The amount of ball clay needed for this purpose depended upon the nature of the china clays. The more non-plastic the china clay, the smaller was the amount of ball clay required to produce a fluid slip. Low viscosity slip could not be prepared with china clay alone. The introduction of a small amount of ball clay resulted in a sharp lowering of the minimum viscosity, and the viscosity continued to fall as the proportion of ball clay was increased. With dark ball clay the lowest viscosity was reached in a slip containing 37.5 per cent ball clay to 12.5 per cent china clay, whereas in the case of the blue ball clay minimum viscosity was attained in an all ball clay slip.

In this connection it should be mentioned that the attainment of minimum viscosity in a slip is not considered of fundamental importance by all workers in this field. Emery[7] is of the opinion that it is not always advisable to use a slip with maximum fluidity or minimum viscosity. The most fluid slips are not necessarily the most desirable. The chief properties to be considered in a casting slip, according to Emery, are the time of casting and the "guarding against flabbiness."

In the matter of controlling these slips it should be noted that attempts have been made in recent years to develop methods based

[5] P. H. Sanborn, "Slip Making and Control," *Jour. Amer. Ceram. Soc.*, Vol. 8 (1925), p. 555.

[6] E. W. Scripture, Jr., and E. Schramm, "The Deflocculation of Clay Slips and Related Properties," *Jour. Amer. Ceram. Soc.*, Vol. 9 (1926), p. 175.

[7] W. Emery, Address in "Symposium on Faults in Alkaline Slip Casting," Publication of the National Council of the Pottery Industry, Stoke-on-Trent, England.

on the measurement of physico-chemical constants of the casting slip. The determinations of viscosity, hydrogen-ion concentration,[6,8] and conductivity values have been proposed as methods of slip control. With the exception of viscosity control, most of the control methods based upon the measurement of physico-chemical constants of the casting slip have met with little or no success. Viscosity control usually succeeds fairly well.

It is very improbable that the determination of hydrogen-ion concentration or conductivity values can be used as a method for slip control. It is true that the isoelectric point depends upon the hydrogen-ion concentration and that the fluidity varies with the hydrogen-ion concentration to a certain extent. However, there can be no exclusive cause and effect relationship between the concentration of hydrogen ions or the total ionic concentration and mobility and the factors which make for satisfactory formation and setting of the slip. There must be factors other than the concentration of hydrogen ions or the total ionic concentration and mobility which are involved in satisfactory slip formation and setting. The possibility remains, however, that all the factors involved in slip formation and setting may vary with the hydrogen-ion concentration or the conductivity, or, what amounts to the same, the resultant of all these factors might vary with the hydrogen-ion concentration or the conductivity. But the probability of the existence of such a state of affairs must be extremely small, and according to Fessler and Kraner it seems not to exist at all.

From the foregoing references it appears probable that the organic matter of ball clay plays an important part in the casting process. The organic matter of clays belongs to the class of protective colloids which also exert a peptizing action. Many protective colloids not only protect a colloidal dispersion already existing but are also active peptizing agents. In this way, substances in mass can be dispersed with a comparatively small expenditure of mechanical energy. Soaps belong to this class of protective colloids which also peptize matter in mass. The detergent power of soap solutions depends upon such a peptization. The sodium salts of protalbic and lysalbic acids are further examples of powerful protective colloids which may also function as peptizing agents. These compounds may be used to bring mercuric oxide and the hydroxides of iron, zinc, and copper into colloidal solution. These same oxides and hydroxides may also be peptized by a protected metal sol such as a palladium sol protected by sodium protalbate.

[8] D. W. Randolph and A. L. Donnenwirth, "Hydrogen-Ion Measurements on Clay Slips," *Jour. Amer. Ceram. Soc.*, Vol. 9 (1926), p. 541.
A. H. Fessler and H. M. Kraner, "Hydrogen-Ion Concentration and Electrical Conductivity of Clay Slips. Part I. Plant Study," *Jour. Amer. Ceram. Soc.*, Vol. 10 (1927), p. 501. "Part II. Laboratory Study," *Ibid.*, p. 592.

Series I: It was decided in the present work to either entirely eliminate the ball clay in making up slips or to use ball clays containing little or no organic matter, and to add the necessary amount of a peptizing protective colloid. Peat[9] and tannic acid were used as peptizing protective colloids. They were added in varying amounts to the typical body noted above. A variation was also made in the sodium carbonate and silicate contents.

A Georgia china clay and a Tennessee ball clay were used in making up the body. The ball clay contained 0.16 per cent organic carbon. BW brand sodium silicate made by the Philadelphia Quartz Company was used throughout this work. Peat and tannic acid were added in amounts equivalent to 0.05, 0.20, and 0.80 per cent of the weight of the above body (per cent in peat and tannic acid calculated as per cent of dry weight of body before the addition of water). The approximate time of casting and the cross-breaking strength of inch bars cast from the slips were determined. The time of setting could only be determined as a rough approximation. As soon as the cast piece felt sufficiently firm to the touch, it was removed from the mold. The cross-breaking strength was determined in the usual way.

Table I gives the data obtained for slips of the above composition using peat as the source of peptizing protective colloid.

TABLE I

PEAT

Per cent electrolyte	Per cent peptizing protective colloid as carbon	Amount of water used (cc.)	Approximate time of setting (min.)	Cross-breaking strength (lb. per sq. in.)
0.25	0.00	400	120	18.7
0.25	0.05	350	120	41.2
0.25	0.20	300	120	39.7
0.25	0.80	300	180	53.1
0.75	0.00	400	60	36.4
0.75	0.05	350	60	56.2*
0.75	0.20	350	60	48.7*

* Cast piece showed coring (balling). The term coring is self-explanatory. A cross-section of the cast piece is not of uniform structure throughout, but contains a core in the center of the piece. The presence of this core is objectionable.

Table II gives the data obtained for slips of the above composition using tannic acid as the source of the peptizing protective colloid.

It was found successful to make up and cast slips using either peat or tannic acid as peptizing protective colloid and a Tennessee ball clay which contains practically no organic matter. In slips containing no peptizing protective colloid which had stood over

[9] The peat used in these experiments was an ordinary (garden) variety which happened to be on hand. A little experimenting should enable one to use whatever peat can be easily obtained.

night, livering was noticed. The addition of a small amount of tannic acid eliminated the livering. (Livering is a condition of the slip in which it is no longer uniformly fluid but appears to have undergone localized coagulation.) The addition of small amounts of peat and tannic acid decreased the amount of water necessary to make up the slips and increased the cross-breaking strength of inch bars cast from the slips. For instance, the addition of 0.20 per cent organic carbon in the form of peat or tannic acid decreased by 25 per cent the amount of water necessary to make up the slip. The addition of both 0.05 per cent and 0.20 per cent organic carbon in the form of peat and tannic acid more than

TABLE II

TANNIC ACID

Per cent electrolyte	Per cent peptizing protective colloid as carbon	Amount of water used (cc.)	Approximate time of setting (min.)	Cross-breaking strength (lb. per sq. in.)
0.25	0.00	400	120	18.7
0.25	0.05	325	150	57.2
0.25	0.20	300	120	50.0
0.25	0.80	315	120	69.5*
0.75	0.00	400	60	37.2
0.75	0.05	350	60	62.7
0.75	0.20	365	90	103.7

* Cast piece showed coring

doubled the cross-breaking strength of inch bars cast from the slips. These small additions of peptizing protective colloid produced no perceptible change in the time of setting. A further increase, however, in the amount of peptizing protective colloid to 0.80 per cent decreased the rate of setting in the case of peat. An addition of peptizing protective colloid equivalent as carbon to 0.20 per cent of the dry weight of the body appears to be approximately the correct amount necessary to attain maximum water economy without retarding the rate of setting. An increase in the concentration of electrolyte was found to increase the rate of setting, but the increased rate of setting was accompanied by a tendency toward coring.

Series II: In the next series the ball clay was eliminated. Peat and tannic acid were added to slips having the following composition:

	(grams)	(grams)
China clay	500	500
Flint	300	300
Feldspar	200	200
Sodium carbonate	1.25	3.75
Sodium silicate	1.25	3.75

Table III gives the data obtained in this experiment using peat as the source of peptizing protective colloid.

TABLE III

PEAT

Per cent electrolyte	Per cent peptizing protective colloid as carbon	Amount of water used (cc.)	Approximate time of setting (min.)	Cross-breaking strength (lb. per sq. in.)
0.25	0.00	450	30	14.8
0.25	0.05	375	30	17.1
0.25	0.20	375	30	18.1
0.25	0.80	390	120	27.9
0.75	0.00	450	15	12.0
0.75	0.05	425	15	17.3
0.75	0.20	375	30	24.0

Table IV gives the data obtained using tannic acid as the source of peptizing protective colloid.

TABLE IV

TANNIC ACID

Per cent electrolyte	Per cent peptizing protective colloid as carbon	Amount of water used (cc.)	Approximate time of setting (min.)	Cross-breaking strength (lb. per sq. in.)
0.25	0.00	450	30	14.8
0.25	0.05	375	30	21.2
0.25	0.20	375	45	44.0
0.25	0.80	400	180	31.6*

* Cast piece showed coring

With this particular china clay it was impossible to cast satisfactorily with 0.75 per cent electrolyte when using tannic acid. The slips did not remain fluid during the over-night interval between the making up and casting of the slip.

It was found possible to make up and cast slips using only this china clay together with a peptizing protective colloid. The results obtained with an English china clay are very similar to the results obtained with Georgia china clay and the Tennessee ball clay. The chief difference in the two bodies is the greatly increased rate of casting obtained when the china clay alone is used. Just as in the case of the body containing both ball and china clays, the addition of a peptizing protective colloid to a body containing only china clay decreases the amount of water necessary and increases the cross-breaking strength of the cast ware. As in the former instance, 0.20 per cent peptizing protective colloid in the form of peat or tannic acid expressed as carbon appears to be approximately the correct amount to add.

It was next proposed to study the liquefying by the incorporation of a peptizing protective colloid in a slip. Tannic acid was used as the peptizing protective colloid. The liquefying effect of tannic acid alone, each electrolyte alone, and of tannic acid together with each electrolyte and with both electrolytes was ob-

served by means of viscosity determinations on a body of the following composition:

	(grams)
English china clay	250
Flint	150
Feldspar	100

NOTE: The electrolyte percentages as well as the variation in water content and tannic acid are all noted on the curves shown in Figs. 1 and 2.

Viscosities were measured with a simple efflux viscosimeter of the type described by Bleininger.[3]

$$\text{Relative viscosity} = \frac{\text{Time of outflow, slip}}{\text{Time of outflow, water}} \times \text{specific gravity of slip}$$

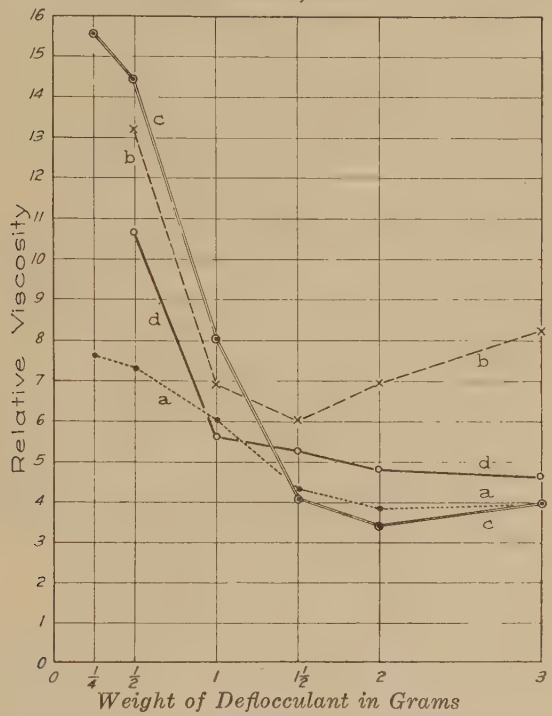

Fig. 1.—Slips of standard compositions with variation in water content.

a Varying weight of sodium carbonate, water 375 cc.
b Varying weight of sodium silicate, water 250 cc.
c Equal weights of sodium carbonate and sodium silicate, water 300 cc.
d Varying weight of tannic acid, water 350 cc.

After the slips had been made up they were allowed to stand over night, and again blunged a short time immediately before making the viscosity determinations.

Comparison of Curves *a* and *b* (Fig. 1) shows that sodium silicate is a more effective deflocculant than sodium carbonate, a

fact noted by McDowell.[10] The silicic acid obtained from the hydrolysis of the sodium silicate may exert a protective action upon the system and thereby at least partially account for the smaller amount of water required when sodium silicate alone is used.

Curve *d* (Fig. 1) shows that tannic acid without electrolyte acts as deflocculant, although not a very effective one, since the amount of water required is relatively large.

Comparison of Curves *e* and *f* (Fig. 2) shows the difference in the liquefying effects of sodium carbonate and sodium silicate when the electrolytes are added to slips containing tannic acid.

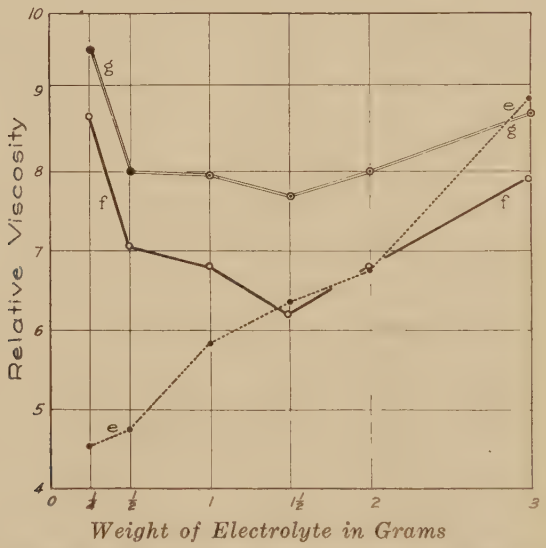

Fig. 2.—Slips of standard composition with addition of 0.5 g. of tannic acid and variation in water content.

e Varying weight of sodium carbonate, water 275 cc.
f Varying weight of sodium silicate, water 250 cc.
g Equal weights of sodium carbonate and sodium silicate, water 250 cc.

In the slip containing sodium carbonate the viscosity steadily increased as the concentration of the sodium carbonate was increased. In the slip containing sodium silicate, after the minimum, the viscosity then increased as the concentration of sodium silicate was increased.

Comparison of Curves *c* (Fig. 1) and *g* (Fig. 2) shows the effect of the addition of tannic acid to a slip containing equal amounts of sodium silicate and sodium carbonate. The incorporation of a peptizing protective colloid decreased the amount of water necessary to make up a slip. The amount of water could undoubt-

[10] S. J. McDowell, "The Effect of Various Sodium Silicates and Other Electrolytes on Clay Slips," *Jour. Amer. Ceram. Soc.*, Vol. 10 (1927), p. 225.

edly be further decreased by increasing the amount of tannic acid added, but continued increase in the amount of tannic acid addition would lead to a decreased rate of setting of the slip.

APPENDIX

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